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Ejection of excimers from the surface of solid argon upon exciton self-trapping

S. T. Cui and R. E. Johnson
Department of Nuclear Engineering and Engineering Physics, University of Virginia, Charlottesville, Virginia 22901

C. T. Reimann
Naval Research Laboratory, Washington, D.C. 20375

J. W. Boring
Department of Nuclear Engineering and Engineering Physics, University of Virginia, Charlottesville, Virginia 22901

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The fate of an excimer (Ar_2^*) formed upon exciton self-trapping is investigated by use of a classical dynamics calculation. It is shown that the triplet excimer, formed by trapping on the surface, may be ejected from the film without significant vibrational relaxation and with a kinetic energy less than 0.1 eV. This ejection is shown to be related to the formation of a "cavity" around an Ar_2^* located in the bulk of solid Ar. At a damaged surface site, vibrationally excited excimers may relax and remain weakly bound to the solid. Following emission of a photon, a ground-state atom is ejected with a kinetic energy of about 0.5 eV, as observed experimentally.

INTRODUCTION

An interesting phenomenon in the field of energetic particle-solid interactions is the conversion of electronically deposited energy (excitons or holes) into kinetic energy of sputtered (desorbed) particles.[1] One case that has been studied extensively is particle ejection from electronically excited solid argon films.[2-6] The vacuum-ultraviolet (VUV) luminescence spectra of the rare-gas films have been shown to be highly correlated with particle ejection,[3-6] a fact that has aided our understanding of the energy conversion processes.

The dominant features of particle ejection and VUV luminescence from solid argon may be understood in terms of the diffusion, trapping, and subsequent decay of holes or atomic excitons, Ar^*, produced by electronic excitation of the solid. These excitons are known to trap at a bulk site[7] or at the surface[8] as atomic self-trapped excitons (Ar^*) or as dimers (Ar_2^*), which have a preferential bond with one nearest neighbor. It is the fate of the latter species and their possible ejection from the surface that interests us in the calculations presented here.

A study of the luminescence produced by low-energy electron excitation of solid argon led Coletti, Debever, and Zimmerer[4] to suggest that ejection of excited Ar^* and Ar_2^* could take place due to a cavity formation mechanism. For example, exciton self-trapping in the bulk to form an excimer Ar_2^* is accompanied by the formation of a cavity as shown in Fig. 1(a). The repulsive forces required to form this cavity near the surface could result in ejection of the enclosed excimer,[4] as indicated in Fig. 1(b). Along with other suggested ejection processes,[3] such an ejection mechanism might be operative for surface-trapped excitons which are produced under any form of electronic excitation, such as bombardment by swift, light ions, electrons, and VUV photons. Whether or not such a mechanism is active is of particular interest due to the recent observation of ejected triplet excimers and the determination of their average kinetic energy.[3]

Recently, we showed in a classical dynamics calculation that atomic excitation trapping at the surface *can* lead to ejection of *excited atoms* from solid Ar,[9] which was subsequently seen experimentally.[10] In this paper potentials are constructed and a classical dynamics calculation is performed in order to test the feasibility of *excited dimer* ejection. In these calculations the distribution of the initial vibrational states of the excimer Ar_2^* is not known at the time of trapping and indeed may be different for different precursor processes. Therefore, we consider two

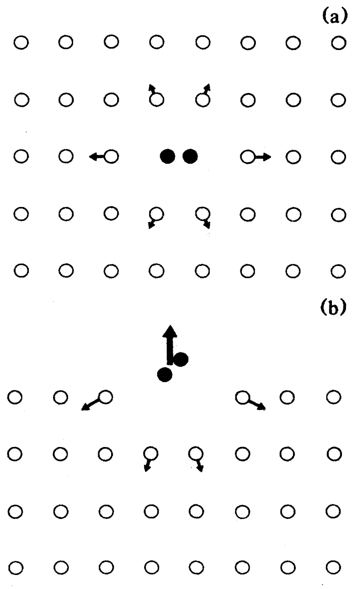

FIG. 1. (a) A two-dimensional schematic diagram of cavity formation in solid argon as viewed for a (110) plane. The excimer is represented by the solid circles. Longer arrows indicate stronger repulsion. (b) The schematic diagram illustrating the ejection of an excimer.

extreme cases, "unrelaxed" and relaxed excimers. It is found here that cavity ejection of excimers *can* contribute to electronically driven ejection of material from the surface of electronically excited, solid Ar films.

THE POTENTIALS AND THE CALCULATION

In the molecular dynamics calculation performed here, the interactions are assumed to be pairwise additive and include interactions with up to the sixth nearest neighbor.[9] The details of the numerical integration (fourth-order predictor-corrector method) are discussed in Ref. 11. For interactions between ground-state atoms, the potential of Aziz and Chen[12] is used. Upon interaction with a neighboring ground-state atom, each excited Ar^* state (singlet or triplet) splits, allowing a number of possible potentials (labeled Σ,Π,g,u). For the first electronic excited state which we consider here, the interaction with the neighbor to form the excimer (excited dimer) is via the attractive ${}^{1,3}\Sigma_u$ potential.[7] The interaction with the other neighbors can be approximated by an average of the other possible excited-state potentials. For a given calculation a pair of nearest neighbors is chosen to form the self-trapped excimer. A Morse potential is used to describe the ${}^{1,3}\Sigma_u$ interaction between the two atoms forming the excimer; the Morse parameters[13] are $D_e=0.664$ eV, $\alpha=2.5898$ Å^{-1}, and $R_e=2.43$ Å.

The interaction between each of the two atoms forming the excimer and the surrounding ground-state atoms is calculated as follows: For internuclear separations greater than $14a_0$, $V=C_6/R^6$ where $C_6=170$ eV Å^6.[9] Beyond 10.2 Å the interaction is set to zero (sixth nearest neighbor). For separations between $6a_0$ and $14a_0$, an average of the interaction potentials between an excited atom in the dimer and a neighboring ground-state atom ($\mathrm{Ar}^*+\mathrm{Ar}$) is calculated excluding the u state involved in bonding of the two atoms in the excimer. The covalent interaction binding the excimer can be thought of as a rapid exchange of an excited state between the two atoms. Thus, the interaction of the excimer with a neighboring atom is the combined effect of the interactions of a ground-state atom *and* an excited-state atom with a ground-state atom. Because the atoms in the system move slowly compared to the excitation transfer within the excimer, the average of excited state ($\mathrm{Ar}^*+\mathrm{Ar}$) and the ground-state (Ar+Ar) potentials is used to describe the *average* pair potential between *each* atom in the excimer and each surrounding atom. We are primarily interested in the triplet excimer ejection energies. However, in order to test the sensitivity of the calculation to the determination of this potential, two potentials are used for $R<14a_0$: the lowest-lying triplet-state interaction V_t and a potential in which the *singlet* and *triplet* state interactions are also averaged, V_a.

In the description of the crystal, the zero-point energy is neglected and the average cohesive energy of the crystal is calculated to be 0.088 eV, a value slightly larger than the known sublimation energy. (Inclusion of the zero-point energy corrects the sublimation energy but changes the ejection energies on the average by $\sim\pm0.01$ eV.) An excimer is "produced" by changing the potentials for a selected pair of neighbors from ground-state values to those constructed above, after which the fate of the atoms in and near the excimer is followed for $\sim10^{-11}$ sec. For the "unrelaxed" excimer the atoms are put in their crystalline configuration while for an excimer formed in the fully relaxed vibrational state, the atomic separation is set to 2.43 Å, the equilibrium separation of the two atoms in the relaxed excimer, while the other atoms are left in the undeformed crystal configuration. The excimer center and orientation coincide with the center and orientation when the atoms are on crystal sites.

The investigation of the possibility of dimer ejection is carried out for two different crystal faces, (100) and (111) with 108 and 180 atoms, respectively. A two-dimensional periodic condition is used, for convenience, for the side boundaries and the face perpendicular to the z direction is the vacuum surface. If an atom or dimer is at least 10.2 Å away from the surface, it is assumed to be sputtered.[11] For the energies and times involved the number of atoms used in the sample and the boundary conditions do not affect the calculated kinetic energy of the ejected species. Further, the accuracy of the integration scheme is such that the calculated kinetic energies have an uncertainty much less than 10^{-3} eV at the end of the run.

RESULTS

The radial expansion of the atoms surrounding a *relaxed* excimer formed in the bulk was calculated. In this calculation the separation of the two atoms in the molecular exciton was fixed to 2.43 Å, the equilibrium separation. Following the subsequent motion of the lattice atoms through a number of oscillations, it was estimated that for the eight neighbors nearest to the center of the excimer, the radial expansion is about 0.4–0.5 Å. This calculation gives a "cavity" energy shift in the bulk of 0.54 eV for V_t and 0.62 eV for V_a. As these values are reasonably close to the estimate based on the luminescence data[3] of about 0.6 eV, the choice of potentials used for the desorption study appears reasonable.

The calculation of the fate of an excimer formed in the surface layer shows that ejection of the excimer happens quickly in times of the order of 10^{-12} sec. Since the "initial" vibrational state of the trapped excimer is not known, and may differ for differing excitation processes, results are calculated for both fully relaxed and "unrelaxed" excimers. During the ejection process it is also found that a vibrationally unrelaxed excimer does not experience any relaxation. (In its release from the crystal its vibrational energy may actually increase slightly.) In Table I, the calculated center-of-mass kinetic energies of ejected excimers, listed for the two different potentials, are seen to be less than 0.1 eV.

It is seen that for the (100) face and the triplet potential, V_t, there is *no ejection* for the excimer *formed* in the fully relaxed state, while unrelaxed excimers are ejected. For the (111) face, by contrast both species are ejected. Because actual desorption experiments do not use perfect crystalline samples, calculations are also performed for which the model surfaces are "damaged" by removing neighbors from the vicinity of the excimers. As the num-

TABLE I. Energies of ejected excimers.[a]

		E_{V_t} (eV)		E_{V_a} (eV)	
Surface	Neighbors	Relaxed	Unrelaxed[b]	Relaxed	Unrelaxed
(100)	All present	· · ·	0.02	0.04	0.07
(100)	2 removed	· · ·	0.01	0.03	0.04
(100)	4 removed	· · ·	0.004	0.02	0.04
(100)	5 removed	· · ·	· · ·		
(100)	6 removed	· · ·	· · ·	0.02	0.03
(100)	1st and 2nd layer	· · ·	· · ·	· · ·	0.04
(111)	All present	0.03	0.02	0.09	0.08
(111)	1st and 2nd layer	· · ·	0.04	0.02	0.06

[a] Dots denote that ejection does not occur.

[b] Unrelaxed implies an excimer formed from two atoms at their equilibrium positions in the crystal.

ber of surface neighbors decreases, the kinetic energy of the ejected excimer decreases due to the decreasing net repulsion. If five or six nearest surface neighbors are removed, there is no ejection of the unrelaxed excimer from the (100) face.

For the fully averaged potential V_a, there is a different behavior with respect to local surface damage than for V_t. For V_a, both the relaxed and the unrelaxed molecular excitons are ejected even if all six nearest surface neighbors are removed. The kinetic energies of the ejected molecular exciton are seen to be lower for the triplet potential V_t than for the fully averaged potential V_a. The differences are due to the slightly weaker repulsion and the deeper potential well of V_t. The singlet-state kinetic energies for ejected dimers would be larger than those for V_a.

Calculations were also performed for an excimer formed from one atom in the first layer and one in the second layer for the (100) face. For this case *no ejection* occurs except for the unrelaxed excimer using V_a. In addition, since the number of neighbors was shown to be important, the results in Table I for the (111) crystal face show stronger repulsion both for excimers formed of the atoms in the same layer and those formed from neighboring layers.

The above results provide an important test of ejection models and contribute to an understanding of recent experimental data. As the excited dimers emit a characteristic light (*W* band), the ejection of the unrelaxed molecular excitons *confirms* that the luminescence recently observed off the surface[3] can have contributions from unrelaxed excimers ejected by the process which also forms cavities in the bulk.[4] However, the calculated kinetic energies of these triplet excimers are low, and it is impossible to account for the kinetic energy of 0.8 eV estimated earlier for ejected excimers.[3] This value for the excimer kinetic energy was estimated by measuring the luminescence intensity versus distance from the surface for the sputtered particles. It was assumed in Ref. 3 that the luminescent plume was due to unrelaxed dimers in the ${}^3\Sigma_u^+$ state being desorbed with a distribution of kinetic energies and with a lifetime of 275 nsec characteristic of the radiation at 11.4 eV.[14] This lifetime was combined with the plume decay length in front of the target, ~0.04 cm,[3] to yield a kinetic energy ~0.8 eV. However, *more detailed* plume data indicate that the triplet decay length is ~0.018 cm for the excimers observed at 11.2 eV, and the component of the *W* band *shifted by* 0.6 eV (10.6 eV) has a plume decay length of 0.038 cm, in agreement with the above. [Note that the fully unrelaxed (11.4 eV) lifetime is 0.275 μsec and the fully relaxed (9.8 eV) lifetime is 1.20 μsec, so that the excimers at 11.2 and 10.6 eV have lifetimes longer than 0.275 μsec.] Assuming a linear increase in lifetime with vibrational relaxation, we obtain similar kinetic energies for these two wavelengths, ~0.1 and 0.12 eV. These kinetic energies are much lower than the 0.8 eV given in Ref. 3 but still somewhat larger than those given in Table I.

The likelihood of excimer ejection was shown to depend on a number of factors: which neighbors are involved in the excimer; the amount of initial vibrational relaxation; the electronic state; and the amount of surface damage. For some of the cases calculated the unrelaxed excimer remains weakly bound to the surface so that additional vibrational relaxation can occur. In such cases the excimer relaxes with a binding minimum ~0.5 Å out from the surface plane. Therefore, the average attraction of the atoms in the excimer to the surface is much weaker than the atomic binding on a perfect crystal surface. (Because of the residual lattice energy these weakly bound relaxed species may eventually also escape.) The possibility of the formation of a relaxed excimer weakly attached to the surface, formed either initially in the trapping process or by relaxation on the surface, can provide an explanation for the structure recently observed in the ejected *atom* kinetic energy spectra.[15–17] In these measurements the ejected-Ar-atom energy spectrum exhibited a feature at very low energies (<0.1 eV) and a peak at about 0.45 eV. The low-energy feature may include contributions from a number of processes discussed elsewhere.[9,15] Upon emission of a photon, the Ar_2^* excimers discussed here end up on the ground-state potential curve. For unrelaxed excimers only a small (<0.1 eV) additional kinetic energy is given to the atoms in the excimers. Therefore, the excimer ejection process above will contribute to the low-energy feature. However, if a relaxed excimer is formed on the surface it eventually emits a photon, ending up on a more repulsive portion of the ground-state potential. For gas-phase argon, this repulsion energy is about 1 eV. A relaxed excimer weakly bound to the surface or ejected would behave as though it is in the gas phase. Therefore, each atom would acquire ~0.5 eV of kinetic energy, a value close to the measured peak position at about 0.45 eV observed in the kinetic energy spectra of Ar atoms ejected from electronically excited solid Ar films.[5,6,15–17] These measurements were initially puzzling as it was shown, using a classical dynamics calculation, that the atoms ejected from excimers decaying in the presence of the full surface binding would have significantly reduced kinetic energies.[15]

CONCLUSIONS

Potentials were constructed for an excimer in solid argon. These were used in a classical dynamics calculation to describe the fate of an excimer (excited dimer Ar_2^*) formed during exciton self-trapping on a solid Ar surface in an unknown state of vibrational relaxation. We have calculated ejection in two extremes, fully relaxed and unrelaxed, and for two approximate potentials. The calculations show that ejection can occur as a consequence of the same repulsive forces that create a cavity around this excimer in bulk Ar.[4] That is, upon self-trapping, the surface excimers can be ejected within $\sim 10^{-12}$ sec with kinetic energies < 0.1 eV. The calculated kinetic energies are much smaller than the total cavity energy shift in the bulk (~0.6 eV), and are somewhat smaller than the kinetic energy implied from the measurements of the triplet component of the W-band luminescent plumes. The promptly ejected excimers leave *without* significant change in their state of vibrational relaxation, so that the vibrationally excited excimers observed in the luminescence plume off the surface are indicative of the state at formation of the excimer. In this regard it would be useful to compare such results for particle excitation to those for photon-excited $(n=1)$ solids for which the W-band plume may be dominated by unrelaxed dimers.

The relaxation on the surface of an initially unrelaxed excimer formed from surface atoms in solid Ar appears unlikely for a perfect or lightly damaged crystal. However, depending on the electronic state, the initial vibrational state, the amount of surface damage, and the neighbors involved in forming the excimer, the resulting repulsion might not be strong enough to cause ejection. Such excimers can undergo vibrational relaxation on the surface, and then decay to the ground state by emitting a photon (~9.8 eV). One of the atoms in this excimer, which is only weakly bound to the surface, would then escape the surface with about half of the repulsive energy found in the ground state, ~0.5 eV as recently observed.[15–17]

These calculations show that the cavity ejection mechanism is a viable process for desorption of the Ar_2^* excimers from electronically excited solid Ar with likely differences in the ejection probabilities and ejection energies for singlet and triplet dimers. This ejection process is only one contribution to the total electronic sputtering yield and we now need to establish the relative importance of this process and the various other processes discussed.[3]

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